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COMPUTER MODELING OF SOOT FORMATION COMPARING FREE RADICAL AND IONIC MECHANISMS

(A Collaborative Effort between AeroChem, Penn State and Iowa State)

H. F. Calcote and Robert J. Gill

AEROCHEM RESEARCH LABORATORIES, INC.
P.O. Box 12
Princeton, New Jersey 08542

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This is the second annual report on a collaborative effort between AeroChem, Penn State, and Iowa State to compare the relative importance of the free radical mechanism of Frenklach and associates and the ionic mechanism of Calcote and associates by use of computer programs run at Penn State and Iowa State. The thermodynamic and reaction kinetics coefficients for the detailed ionic reaction mechanism are being developed by correlating data in the literature and performing theoretical calculations. Comparison of the computer model, using the present set of rate coefficients, with experimental ion concentrations in the standard acetylene-oxygen flame at 1.67 kPa demonstrates a number of problems with the present set of rate coefficients. These are being corrected. A comparison of the time it takes for the neutral and ionic mechanisms, using experimental species concentrations and typical rate coefficients used in the two respective mechanisms, demonstrates that the time to add ten carbon atoms, from C_{10} to C_{20}, by the two mechanisms is comparable. The

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higher concentration of neutral species is balanced by the greater reaction rate coefficients for ion-molecule reactions, and the fewer number of steps involved in adding a specific number of carbon atoms to the growing species for the ionic mechanism than for the neutral mechanism. This analysis demonstrates the need to go to larger species than C_{20} to determine the relative rates of the two mechanisms in producing large carbon species.

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I. INTRODUCTION

This is the second annual report on this program which is a collaborative effort between AeroChem (Principal Investigator: H. F. Calcote), Penn State (Principal Investigator: M. Frenklach) and Iowa State (Principal Investigator: Robert C. Brown). The ultimate objective is to develop a quantitative model of soot formation in flames that is consistent with experimental data. The specific objectives of this collaborative three-year study are: (1) to delineate the relative importance of the neutral free radical and ionic mechanisms of soot formation in flames; (2) to determine the optimum model of the total soot formation process based upon what is currently known; and (3) to recommend what is required to improve the model and what additional experiments are necessary to clarify any discrepancies.

Professor Robert Brown, Iowa State University, has just been added as a collaborator to this program via a subcontract from AeroChem with funds which were added to this program for that purpose. He brings to the program previous experience in developing a code for modeling ionic reactions in flames[1,2] involving the solution of the stiff equations involved in such reactions. He also plans to include ambipolar diffusion in his model; experimentally this has been demonstrated to be very important.[3] The method Brown plans to employ will solve the Poisson equation for electric field strength as a function of one-dimensional charge distribution in the flame. His computer program should allow us to go to larger species than is now possible which appears to be important, see Section V below.

In this report, the AeroChem effort is reviewed; the Penn State effort will be covered in their companion report[4]; it is premature to report on the Iowa State results. AeroChem is responsible for development of the thermodynamics, diffusion coefficients, reaction mechanism, and reaction rate coefficients for the ionic mechanism. There were no previous sets of data on the ionic mechanism to draw upon when we initiated this program; two papers were subsequently published by Brown and Eraslan,[1,2] in which they calculated the concentrations of ions in both stoichiometric and fuel rich flames and compared the calculations with experiments. For the sooting flames we wished to model in this program, it has been necessary not only to construct the ionic mechanism and identify the rate coefficients but also to develop neutral mechanisms and to organize data for odd number neutral carbon compounds. Such species are not generally utilized in the free radical mechanisms of soot formation. Odd carbon neutral species, however, play a significant role in the ionic mechanism and are observed in relatively large concentrations in sooting flames.

The computer modeling results are being compared with the well-documented acetylene/oxygen flame (the "standard flame") burning on a flat flame burner at a pressure of 1.67 kPa (20 Torr) and a linear flow rate of 50 cm/s in the unburned gases. In our previous AFOSR contract work,[3,5,6] we duplicated the burner Bittner and Howard[7] used to obtain neutral species concentrations and we measured ion concentration profiles with this burner so that the ion profiles and the neutral profiles would be from the same system. We also compared the data

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obtained by a number of other researchers on very nearly the same flame; we previously presented the results of this comparison[3] which showed amazing agreement among several laboratories. This data base forms an excellent experimental standard with which to compare the computer modeling results.

II. STATEMENT OF WORK

A. Organize relevant data on ion-molecule reactions, thermochemistry, electron attachment, ion recombination, and ion and electron diffusion to be used in the computer codes.

B. Determine the hydrogen atom concentration in the "well-studied" C_2H_2/O_2 flame and determine if this concentration exceeds the thermal equilibrium concentration.

C. Analyze the computer simulation data obtained by Penn State and Iowa State and compare the results with available experimental data to determine the major chemical pathways to incipient soot and to simplify the computer model.

D. Organize relevant data on the elementary steps involved in the growth of incipient soot to soot particles, including growth by molecular addition, coagulation, and oxidation.

E. Analyze the computer simulation data obtained by Penn State and Iowa State using the extended model and compare the results with available experimental data to determine the major pathways to particulate soot and to determine how to alter the model to make it more in conformity with experimental results.

F. Review the literature and choose flame experiments with which to compare the model developed above.

G. Analyze the computer simulation data obtained by Penn State and Iowa State and compare the results with the experimental data to determine the general applicability of the model and to recommend what is required to improve the model and what additional experiments are necessary to clarify any discrepancies.

The statement of work for the subcontract with Brown at Iowa State is:

A. Incorporate reaction mechanism and thermochemical data developed at AeroChem Research Laboratories in the TRANSEQI computer code.

B. Assess the utility of determining ambipolar diffusion by numerical solution of the Poisson equation using a sample ion model.

. · C.   Perform baseline simulations of a test flame.

D.   Perform numerical simulations of the standard acetylene/oxygen flame.

III. THERMODYNAMICS

The thermodynamic work was reported on in detail in the last report[8] and will not be elaborated on here. The inaccuracy of thermodynamic data continues to contribute a major question in any reaction kinetics scheme. During this report period we have added a few new species to our data base and have reevaluated some of the data. We plan to publish, probably with Steve Stein at NIST, a compilation of the data we have both generated on large ions. Where the ions overlapped, the agreement has been good except for the perinaphthalene ion, $C_{13}H_9^+$. These estimates are $\Delta H_f(298) = 1115$ kJ/mol (298) and 917 kJ/mol, depending upon whether the ion is anti-aromatic or not, respectively. Since $C_{13}H_9^+$ is a very dominant ion in flames and shows up repeatedly in ion spectra,[9] the lower value is probably correct.

IV. REACTION MECHANISM AND REACTION COEFFICIENTS

The present mechanism has recently been run by M. Frenklach and H. Wang at Penn State and has not been completely analyzed so only qualitative interpretations will be given. It is certainly premature to make any judgment from the computer runs made to date. They have mostly been concerned with matching the computer program and the ionic mechanism. The basic problems appear to have been solved so that, in the near future, effort can be made to match the ionic mechanism to experimental data as has been done for the neutral mechanism.[4]

Our emphasis in this report will be on the limitations in the ionic mechanism and what specific work is being done. The neutral part of the mechanism which furnishes the reactants important in the ion-molecule reaction steps are the same as in the neutral mechanism except for the steps added last year to account for the odd number of carbon neutral species which are observed in flames and were added to the neutral mechanism.[8] Thus, we will not discuss this part of the mechanism.

A.   EXCITED STATE/CHEMIIONIZATION

Those specific reactions which produce excited CH, (CH$^{\bullet}$), important in the chemiionization process, and the chemiionization steps are presented in Table I. Probably the two most important reactions in this set (a sensitivity analysis has yet to be analyzed), are Reactions (3) and (9). The rate coefficient for Reaction (3) was estimated by W. Gardiner[10] and the rate coefficient for Reaction (9) was measured by Cool relative to the rate coefficient for Reaction

· (7).[11] The reaction coefficients for Reactions (7) and (8) are from a bimolecular quantum RRK theory calculation by Westmoreland and are in agreement with experiment.[12,13]

B.   ION-MOLECULE REACTIONS

The present set of ion-molecule reactions, chosen from a set of about 250 reactions, is presented in Table II. There were two criteria for the choice: (1) only neutral reactants: C_2H_2, C_4H_2, C_3H_2, C_3H_4 and H_2O were used; (2) only reactions with a negative free energy over the temperature range from the initial temperature to the observed maximum flame temperature were used. The second criterion was employed to avoid difficulties which were experienced with previous sets of data; the reverse reactions turned out to be unrealistically fast. While this device avoided the problem, it probably led to smaller forward rates than are realistic--see Section V. The concentration of acetylene is so much greater than any other potential neutral reactant, that anything other than acetylene as a growth species can probably be ignored, as in soot growth, without a great loss in ion growth rate. Considering acetylene as the only reactant will involve reducing some of the rate coefficients to avoid excessive reverse reaction rates at high temperatures. In general, in the way we have chosen to write the reactions, always toward increasing molecular size, the free energy of reaction becomes more positive as the temperature is increased.

When available, experimental rate coefficients were used, but these are available only for small ions. In general, experimental rates are very close to the rate calculated by the average dipole orientation, ADO, theory[14]

$$k = \frac{2\pi e}{\mu^{1/2}} \left[\alpha^{1/2} + C\mu_D \left(\frac{2}{\pi kT} \right)^{1/2} \right] \tag{1}$$

where, μ is the reduced mass, α is the polarizability of the neutral reactant, C is a locking constant determined from experimental data, and μ_D is the dipole moment of the neutral reactant. For nonpolar species such as the neutral growth species in our ionic model, except for propyne, Eq. (1) reduces to the Langevin equation which does not have a temperature coefficient.

There have been several theoretical analyses with the objective of defining the temperature effect on ion-molecule reactions but these have all concentrated on the situation when the neutral reactant has a dipole moment.[15-20] In the Langevin theory,[21] which forms the basis for these analyses, the ion is treated as a point charge. This is certainly not true for many of the large ions; even when the charge is localized it would be shielded from the approaching reactant by the rest of the molecule. Intuitively the larger ions should have a smaller rate coefficient and a negative temperature coefficient; the theoretical basis has to be developed.

Equation (1) accounts only for the number of collisions (it does not include collision efficiency) and fits most room temperature experimental rate coefficient data. There is considerable evidence that the rate of ion-molecule reactions is directly dependent upon the exothermicity of the reaction, ΔH_r and we hope to use such correlations to estimate the collision efficiency for this set of reactions but have not yet devised a logical means.

One of the major problems in working with large ions is their identification; mass spectrometry gives mass only. The number of carbon and hydrogen atoms has been determined by use of isotopes.[3] Thus for a given molecular formula there can be several isomeric structures. We thus include several isomers for some ions when their free energies of formation are close; we seek a rational means of reducing this to "one isomer" per ion, probably by weighting the thermodynamic quantities, ΔH_f and C_p appropriately and by mechanistic considerations.

Our efforts to assemble an ion-molecule reaction mechanism for soot formation have identified a number of areas where additional fundamental work is required.

C.   ION-ELECTRON RECOMBINATION

The ions disappear by either ion-electron or positive ion-negative ion recombination reactions. Negative ion recombination rate coefficients are about an order of magnitude slower than electron recombination rate coefficients. Further, negative ion concentrations which have been measured are about two orders of magnitude smaller than electron concentrations[22] but there are no good measurements of electron concentrations or negative ions in soot forming flames. There is, however, evidence for the presence of large negative ions in soot forming flames.[3,23] We neglect negative ions for the present; should the ion decay be observed in the model to exceed that observed experimentally, we will reconsider the negative ion possibility. The ion-electron mechanism and rate coefficients are presented in Table III.

In choosing product channels for the large ion-electron dissociative recombination reactions, only molecules observed by Bockhorn et al.[24] have been considered as products. Reaction rate coefficients for ion-electron reactions are not strongly temperature dependent, but they do increase with the size of the ion.

We estimate the rate of ion recombination, α, by the equation for the rate of collision of electrons with particles[25]

$$\alpha = \frac{\pi d^2}{4} \left[\frac{8kT}{\pi m_e} \right]^{1/2} \left[1 + \frac{e^2}{(2\pi\epsilon_0 d)kT} \right] \tag{2}$$

in which d = the ion diameter, m_e = the electron mass, and ϵ_0 = dielectric constant of free space. The ion diameters were calculated from ion mobilities by use of the Langevin equation

·for ion mobilities. Equation (2) gives a $T^{-1/2}$ temperature dependence which compares favorably with experiments of Ogram et al.[26] for H_3O^+. The values calculated by Eq. (2) were about twice the measured values of Ogram, so we have divided the calculated values by 2.

If there is an error in the data in Table III, it will be on the high side. This will be determinable by comparing experiment and computer runs. The computer run should be consistent, if we are correct above, with an interpretation that for smaller ions the recombination coefficients are correct and for larger ions they are too large. Generally, in the computer runs to date,[4] most large ions--there are exceptions--are computed to have far too small a concentration and a more rapid decay rate than observed experimentally. The small concentration may be due to the ion-molecule rates being too small, or due to too fast a loss rate by ion-electron recombination. This could indicate the presence of significant concentrations of negative ions; their rates of recombination are smaller than for electrons. Of course, the recombination of a large positive ion and a large negative ion would double the size of the carbon species, albeit neutral, and could be interpreted as the first step in coagulation. Such collisions are favored, by electric charge effects, over ion-neutral or neutral-neutral collisions.

V. COMPARISON OF THE RATE OF CARBON SPECIES GROWTH FOR NEUTRAL AND IONIC MECHANISMS

The main objective of this program is to compare the rate of formation of large carbon species, which presumably lead to soot, by the free radical mechanism and the ionic mechanism. We have performed a comparison of the two rates by an oversimplified means, but one which should be quite accurate. Experimental measurements of concentrations of both neutral and ionic species in the standard acetylene flame[27] were combined with the rate coefficients for the growth of that species to the next larger species in the sequence, and a time was calculated for each of these steps. The times for the species to add a specified number of carbon atoms by the two mechanisms was then compared. Thus, for the reaction:

$$A + B \rightarrow C + D$$
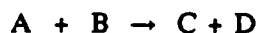
the rate of reaction is given by:

$$R = \frac{dC}{dt} = kAB \tag{3}$$

For this analysis we use the maximum (with respect to distance from the burner) experimental concentrations of A, and use the measured value of B at the position in the flame where the concentration of A is maximum. The appropriate rate coefficient for k is used for either the free radical or the ionic mechanism. In the free radical mechanism,[28,29] A is a stable

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species or a free radical and C is a free radical with the same number of carbon atoms as A, or a stable species with two more carbon atoms than A; B is a hydrogen atom or acetylene. In the ionic mechanism, A is an ion and C is an ion with two more carbon atoms than A; B is acetylene.

The time for a number, n, of the same species per unit volume to react is:

$$r = n/R. \tag{4}$$

where R is the appropriate rate constant for that step.

For this exercise, we chose n as the maximum soot number density observed in this flame, 4×10^9 cm^{-3}. The number is not important for the comparison, but, as we will see, the use of the maximum number of soot particles has interesting implications. Thus we write the mechanism for adding ten carbons in the free radical mechanism and in the ionic mechanism, Tables IV and V, respectively. The time for each step is calculated by Eq. (4) using the free radical rate coefficients from Frenklach et al.[29]:

for A + H$\cdot$ (-H$_2$) $k = 1 \times 10^{14}$ cm^3 mol^{-1} s^{-1}

and   for A + C$_2$H$_2$ (-H$\cdot$) $k = 1 \times 10^{13}$

and the ion-molecule reaction rate coefficient:

for A$^+$ + C$_2$H$_2$ (-D) $k = 6 \times 10^{14}$.

In calculating the reaction times, only the forward reactions are considered for both mechanisms.

The total times required to add ten carbon atoms, Tables IV and V, are comparable for the two mechanisms: 9.7 μs for the free radical mechanism and 5.6 μs for the ionic mechanism. The higher concentration of neutral species is balanced by the greater reaction rate coefficients for ion-molecule reactions and the fewer number of steps involved in addimg a specific number of carbon atoms to the growing species for the ionic mechanism than for the neutral mechanism.

Consideration for larger carbon containing species is not possible for the free radical mechanism because experimental data on large neutral species are not available in the standard flame, presumably because the concentrations are below detection limits. In fact, in the calculations of reaction times reported in Table IV, the neutral species concentrations above $C_{14}H_8$ were estimated from measurements in a different flame[24] because they are not available in the standard flame. Note the decrease in maximum concentration in going from C_6H_6 to $C_{14}H_8$ in the standard flame:

benzene	C_6H_6	7.8×10^{12} per cm^{-3}
naphthalene	$C_{10}H_8$	1.8×10^{11}
ethynylnaphthalene	$C_{12}H_8$	6.9×10^{10}
	$C_{14}H_8$	1.7×10^{10}

This is a decrease in concentration of about a factor of 60 per carbon atom added. Bockhorn's results,[24] which cover a larger range of carbon species do not indicate such a rapid decay, but unfortunately they are in a different flame.

For ions the decay in concentration is much less,[3] e.g.:

$C_3H_3^+$	4.7×10^8 per cm^{-3}
$C_{30}H_{15}^+$	1.9×10^7
$C_{45}H_{17}^+$	1.9×10^6

This is a decrease in concentration of about a factor of 6 per carbon atom added, about one-tenth that indicated above for neutral species!

Clearly a comparison of the two mechanisms requires extension to much larger species than is done in Tables IV and V. The computer modeling effort will thus have to be extended to greater masses than are currently in the computer model.

We now consider the implications of the above calculations of reaction times. The maximum concentration of soot number density is reached at about 35 mm above the burner, or about 6.7 ms from the position in the flame at which large carbon containing species maximize. This is a good estimate of the time available, τ_s, for soot particles to be formed from molecular species. If we assume the time for addition of one carbon atom to the growing species is τ_c, then the number of carbon atoms, N_c, that can be added to the growing nuclei is:

$$N_c = \frac{\tau_s}{\tau_c} = \frac{6.7 \times 10^{-3}}{7.4 \times 10^{-7}} \approx 9,000 \text{ carbon atoms.}$$

τ_c is taken as the average for the neutral and ion mechanisms, Table IV and V. 9,000 carbon atoms corresponds to a molecular weight of about 110,000 amu. This is equivalent to a particle diameter of about 4.5 or 3.0 nm, depending upon whether the particle is planar or spherical, respectively.[30] The experimentally observed particle diameters at 35 mm above the burner surface are 9-13 nm for neutral particles and 3-6 nm for charged particles. One of the interesting observations is that the calculated diameter, assuming the equivalent of a fixed rate (fixed time) for adding carbon atoms to the growing species, neutral or ion, leads to a diameter of the carbon particle very close to that observed, within the accuracy of the calculation and the measurement.

The main point of the above discussion with respect to our primary objective, is that examining relatively small carbon species does not permit a decision between the rate of soot nucleation by the neutral and the ionic mechanism; they both have about the same reaction times with the data that have been analyzed. To make a distinction between the two mechanisms one must examine reactions involving larger numbers of carbon atoms than are in the present computer model.

VI. PUBLICATIONS

A publication of the thermodynamic data base developed for this program will probably be submitted for publication with Steve Stein at NIST who has also developed thermodynamic data on large ions, a few overlapping ours. A manuscript will be submitted to Blackwell who is publishing the plenary lectures of the Third International Seminar on Flame Structure at Alma Ata (USSR), September 1989. Our title was "The Role of Ions in Soot Formation"; the subject matter of Section V of this report was presented.

VII. PROFESSIONAL PARTICIPATION

The Principal Investigator on the program is H. F. Calcote who has been responsible for developing the reaction mechanism and collecting the reaction kinetics data. Dr. R. J. Gill has been responsible for collecting and calculating the thermodynamics data. We both acknowledge fruitful discussions with Drs. W. Felder and D. G. Keil.

VIII. TECHNICAL INTERACTIONS

During this period Prof. Phil Westmoreland and his student visited AeroChem to consult with us on their setting up a mass spectrometer to study flames (incidently ours is idle !). We have consulted with a number of people from whom we have solicited help in setting up our mechanism. These have included: William Gardiner; Dave Golden; Sharon G. Lias; Steve Stein; and Phil Westmoreland.

IX. INVENTIONS

None.

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TABLE I

EXCITED STATE/CHEMIIONIZATION REACTIONS

$$k = AT^n \exp(-E(kJ)/RT), \; cm^3, \; mol, \; s$$

No.	REACTION		A	n	E, kJ
1	$C_2 + OH$	$\rightarrow CH(^2\Delta) + CO$	3.4E+12	0.0	0
2	$C_2H + 0$	$\rightarrow CH(^2\Delta) + CO$	7.1E+11	0.0	0
3	$C_2H + O_2$	$\rightarrow CH(^2\Delta) + CO_2$	4.5E+15	0.0	105
4	$CH(^2\Delta) + M$	$\rightarrow CH(^2\Pi) + M$	4.0E+10	0.5	0
5	$CH(^2\Delta) + O_2$	$\rightarrow CH(^2\Pi) + O_2$	2.4E+12	0.5	0
6	$CH(^2\Delta)$	$\rightarrow CH(^2\Pi)$	1.7E+05	0.0	0
7	$CH(^2\Pi) + 0(^3P)$	$\rightarrow HCO^+ + e$	4.6E+08	0.73	-2.56
8	$CH(^2\Pi) + 0(^3P)$	$\rightarrow H + CO$	3.1E+14	-0.25	1.1
9	$CH(^2\Delta) + 0(^3P)$	$\rightarrow HCO^+ + e$	4.8E+14	0.0	0

TABLE II

ION-MOLECULE REACTIONS

$$k = AT^n \exp(-E(kJ)/RT), \text{ cm}^3, \text{ mol, s}$$

Codes for molecular structure: $C_3H_3^+ = C_3H_3^+(1)$; $H_3C_3^+ = C_3H_3^+(c)$; $C_3H_4 = C_3H_4(\text{allene})$; $H_4C_3 = C_3H_4(\text{propyne})$; $C_6H_5^+ = C_6H_5^+(\text{linear})$; $C_2H_3 = C_2H_3(1)$; $C_7H_7^+ = \text{benzyl}$; $C_3H_2 = H\text{-}C\text{=}C\text{=}CH$; $HC = CH^*$ (electronic state: $^2\Delta$); $C_xH_y^+$, $H_yC_x^+$, and $C_xH_{(y-n)}H_n$ represent three different isomers of the same ion.

No.	REACTION				A	n	E, kJ
1	HCO^+	$+ C_2H_2$	$= C_2H_3^+$	$+ CO$	8.3E+14	0.0	0
2	HCO^+	$+ C_3H_2$	$= C_3H_3^+$	$+ CO$	7.3E+14	0.0	0
3	HCO^+	$+ C_3H_4$	$= C_3H_3^+$	$+ H_2 + CO$	7.0E+14	0.0	0
4	HCO^+	$+ C_4H_2$	$= C_4H_3^+$	$+ CO$	6.0E+14	0.0	0
5	HCO^+	$+ H_2O$	$= H_3O^+$	$+ CO$	1.9E+15	0.0	0
6	H_3O^+	$+ C_4H_2$	$= C_4H_3^+$	$+ H_2O$	8.6E+14	0.0	0
7	H_3O^+	$+ C_3H_2$	$= C_3H_3^+$	$+ H_2O$	8.6E+14	0.0	0
8	$C_2H_3^+$	$+ C_2H_2$	$= C_4H_3^+$	$+ H_2$	3.0E+14	0.0	0
9	$C_3H_3^+$	$+ C_3H_4$	$= C_4H_3^+$	$+ C_2H_4$	6.6E+14	0.0	0
10	$C_3H_3^+$	$+ C_3H_4$	$= C_4H_5^+$	$+ C_2H_2$	7.5E+14	0.0	0
11	$C_3H_3^+$	$+ C_4H_2$	$= C_5H_3^+$	$+ C_2H_2$	8.4E+14	0.0	0
12	$C_3H_3^+$	$+ C_2H_2$	$= C_5H_3^+$	$+ H_2$	3.0E+14	0.0	0
13	$C_3H_3^+$	$+ C_3H_4$	$= C_6H_5^+$	$+ H_2$	6.6E+14	0.0	0
14	$C_3H_3^+$	$+ M$	$= H_3C_3^+$	$+ M$	3.2E+15	0.0	0
15	$C_3H_3^+$	$+ OH$	$= HCO^+$	$+ C_2H_3$	7.6E+14	-0.1	125
16	$C_4H_3^+$	$+ C_3H_4$	$= C_7H_7^+$		6.0E+14	0.0	0
17	$C_4H_3^+$	$+ C_3H_4$	$= C_7H_5^+$	$+ H_2$	7.6E+14	0.0	0
18	$C_4H_5^+$	$+ C_2H_2$	$= C_6H_5^+$	$+ H_2$	6.0E+14	0.0	0
19	$C_4H_5^+$	$+ C_4H_2$	$= C_8H_7^+$		6.0E+14	0.0	0
20	$C_4H_5^+$	$+ C_3H_4$	$= C_7H_7^+$	$+ H_2$	6.0E+14	0.0	0
21	$C_5H_3^+$	$+ C_3H_4$	$= C_6H_5^+$	$+ C_2H_2$	6.6E+14	0.0	0
22	C_6H_5+	$+ C_3H_4$	$= C_7H_7^+$	$+ C_2H_2$	6.5E+14	0.0	0
23	$C_6H_5^+$	$+ C_3H_4$	$= C_9H_7^+$	$+ H_2$	6.0E+14	0.0	0
24	$C_7H_5^+$	$+ C_3H_4$	$= C_8H_7^+$	$+ C_2H_2$	6.0E+14	0.0	0

TABLE II (continued)

No.	REACTION	A	n	E, kJ
25	$C_7H_5^+$ + C_3H_4 = $C_{10}H_9^+$	6.0E+14	0.0	0
26	$C_7H_5^+$ + C_3H_4 = $H_9C_{10}^+$	6.0E+14	0.0	0
27	$C_7H_5^+$ + C_2H_2 = $C_9H_7^+$	6.0E+14	0.0	0
28	$C_7H_7^+$ + C_3H_4 = $C_{10}H_9^+$ + H_2	6.0E+14	0.0	0
29	$C_8H_7^+$ + C_2H_2 = $C_{10}H_9^+$	6.0E+14	0.0	0
30	$C_8H_7^+$ + C_4H_2 = $C_{12}H_9^+$	6.0E+14	0.0	0
31	$C_8H_7^+$ + C_3H_4 = $H_9C_{11}^+$ + H_2	6.0E+14	0.0	0
32	$C_9H_7^+$ + C_3H_4 = $C_{10}H_9^+$ + C_2H_2	6.0E+14	0.0	0
33	$C_9H_7^+$ + C_3H_4 = $H_9C_{10}^+$ + C_2H_2	6.0E+14	0.0	0
34	$C_{10}H_9^+$ + C_2H_2 = $C_{12}H_9^+$ + H_2	6.0E+14	0.0	0
35	$C_{10}H_9^+$ + C_4H_2 = $C_{12}H_9^+$ + C_2H_2	6.0E+14	0.0	0
36	$C_{11}H_9^+$ + C_2H_2 = $C_{13}H_9^+$ + H_2	6.0E+14	0.0	0
37	$C_{11}H_9^+$ + C_2H_2 = $C_{13}H_8H^+$ + H_2	6.0E+14	0.0	0
38	$C_{11}H_9^+$ + C_4H_2 = $C_{13}H_9^+$ + C_2H_2	6.0E+14	0.0	0
39	$C_{11}H_9^+$ + C_4H_2 = $C_{13}H_8H^+$ + C_2H_2	6.0E+14	0.0	0
40	$C_{12}H_9^+$ + C_4H_2 = $C_{16}H_{11}^+$	6.0E+14	0.0	0
41	$C_{13}H_9^+$ + C_4H_2 = $C_{17}H_{11}^+$	6.0E+14	0.0	0
42	$C_{13}H_9^+$ + C_4H_2 = $H_{11}C_{17}^+$	6.0E+14	0.0	0
43	$C_{15}H_{11}^+$ + C_2H_2 = $C_{17}H_{11}^+$ + H_2	6.0E+14	0.0	0
44	$C_{15}H_{11}^+$ + C_4H_2 = $C_{17}H_{11}^+$ + C_2H_2	6.0E+14	0.0	0
45	$C_{15}H_{11}^+$ + C_4H_2 = $H_{11}C_{17}^+$ + C_2H_2	6.0E+14	0.0	0
46	$C_{15}H_{11}^+$ + C_2H_2 = $H_{11}C_{17}^+$ + H_2	6.0E+14	0.0	0
47	$C_{16}H_{11}^+$ + C_4H_2 = $H_{11}C_{20}^+$ + H_2	6.0E+14	0.0	0
48	$C_{17}H_{11}^+$ + C_4H_2 = $C_{19}H_{11}^+$ + C_2H_2	6.0E+14	0.0	0
49	$C_{17}H_{11}^+$ + C_2H_2 = $C_{19}H_{11}^+$ + H_2	6.0E+14	0.0	0
50	$C_{17}H_{11}^+$ + C_4H_2 = $C_{21}H_{11}^+$ + H_2	6.0E+14	0.0	0
51	$C_{18}H_{11}^+$ + C_2H_2 = $C_{20}H_{11}^+$ + H_2	6.0E+14	0.0	0
52	$C_{18}H_{11}^+$ + C_4H_2 = $C_{20}H_{11}^+$ + C_2H_2	6.0E+14	0.0	0
53	$C_{18}H_{11}^+$ + C_4H_2 = $C_{22}H_{13}^+$	6.0E+14	0.0	0
54	$C_{18}H_{11}^+$ + C_2H_2 = $H_{11}C_{20}^+$ + H_2	6.0E+14	0.0	0

TABLE II (continued)

No.	REACTION	A	n	E, kJ
55	$C_{18}H_{11}^+ + C_4H_2 = H_{11}C_{20}^+ + C_2H_2$	6.0E+14	0.0	0
56	$C_{19}H_{11}^+ + C_4H_2 = C_{21}H_{11}^+ + C_2H_2$	6.0E+14	0.0	0
57	$C_{19}H_{11}^+ + C_2H_2 = C_{21}H_{11}^+ + H_2$	6.0E+14	0.0	0
58	$C_{19}H_{11}^+ + C_3H_4 = C_{22}H_{13}^+ + H_2$	6.0E+14	0.0	0
59	$C_{20}H_{11}^+ + C_2H_2 = C_{22}H_{13}^+$	6.0E+14	0.0	0
60	$C_{20}H_{11}^+ + C_3H_4 = C_{23}H_{13}^+ + H_2$	6.0E+14	0.0	0
61	$C_{20}H_{11}^+ + C_4H_2 = C_{24}H_{13}^+$	6.0E+14	0.0	0
62	$C_{21}H_{11}^+ + C_3H_4 = C_{22}H_{13}^+ + C_2H_2$	6.0E+14	0.0	0
63	$C_{21}H_{11}^+ + C_3H_4 = C_{24}H_{13}^+ + H_2$	6.0E+14	0.0	0
64	$C_{22}H_{13}^+ + C_2H_2 = C_{24}H_{13}^+ + H_2$	6.0E+14	0.0	0
65	$C_{22}H_{13}^+ + C_4H_2 = C_{24}H_{13}^+ + C_2H_2$	6.0E+14	0.0	0
66	$H_9C_{10}^+ + C_2H_2 = C_{12}H_9^+ + H_2$	6.0E+14	0.0	0
67	$H_9C_{10}^+ + C_2H_2 = H_9C_{12}^+ + H_2$	6.0E+14	0.0	0
68	$H_9C_{10}^+ + C_3H_4 = C_{13}H_8H^+ + H_2 + H_2$	6.0E+14	0.0	0
69	$H_9C_{10}^+ + C_3H_4 = C_{13}H_9^+ + H_2 + H_2$	6.0E+14	0.0	0
70	$H_9C_{10}^+ + C_4H_2 = C_{12}H_9^+ + C_2H_2$	6.0E+14	0.0	0
71	$H_9C_{10}^+ + C_4H_2 = H_9C_{12}^+ + C_2H_2$	6.0E+14	0.0	0
72	$H_9C_{11}^+ + M = C_{11}H_9^+ + M$	1.0E+14	0.0	0
73	$H_9C_{11}^+ + C_2H_2 = C_{13}H_8H^+ + H_2$	6.0E+14	0.0	0
74	$H_9C_{11}^+ + C_4H_2 = C_{13}H_8H^+ + C_2H_2$	6.0E+14	0.0	0
75	$H_9C_{11}^+ + C_4H_2 = C_{13}H_9^+ + C_2H_2$	6.0E+14	0.0	0
76	$H_9C_{12}^+ + C_3H_4 = C_{15}H_{11}^+ + H_2$	6.0E+14	0.0	0
77	$H_9C_{12}^+ + C_4H_2 = C_{16}H_{11}^+$	6.0E+14	0.0	0
78	$C_{13}H_8H^+ + C_3H_4 = H_{11}C_{16}^+ + H_2$	6.0E+14	0.0	0
79	$C_{13}H_8H^+ + C_3H_4 = C_{16}H_{11}^+ + H_2$	6.0E+14	0.0	0
80	$C_{13}H_8H^+ + C_4H_2 = H_{11}C_{17}^+$	6.0E+14	0.0	0
81	$C_{13}H_8H^+ + C_4H_2 = C_{17}H_{11}^+$	6.0E+14	0.0	0
82	$H_{11}C_{16}^+ + C_2H_2 = H_{11}C_{18}^+ + H_2$	6.0E+14	0.0	0
83	$H_{11}C_{16}^+ + C_2H_2 = C_{18}H_{11}^+ + H_2$	6.0E+14	0.0	0
84	$H_{11}C_{16}^+ + C_4H_2 = H_{11}C_{20}^+ + H_2$	6.0E+14	0.0	0

TABLE II (continued)

No.	REACTION	A	n	E, kJ
85	$H_{11}C_{16}^+ + C_4H_2 = H_{11}C_{18}^+ + C_2H_2$	6.0E+14	0.0	0
86	$H_{11}C_{16}^+ + C_4H_2 = C_{18}H_{11}^+ + C_2H_2$	6.0E+14	0.0	0
87	$H_{11}C_{16}^+ + C_4H_2 = C_{20}H_{11}^+ + H_2$	6.0E+14	0.0	0
88	$H_{11}C_{17}^+ + C_2H_2 = C_{19}H_{11}^+ + H_2$	6.0E+14	0.0	0
89	$H_{11}C_{17}^+ + C_4H_2 = C_{19}H_{11}^+ + C_2H_2$	6.0E+14	0.0	0
90	$H_{11}C_{17}^+ + C_4H_2 = C_{21}H_{11}^+ + H_2$	6.0E+14	0.0	0
91	$H_{11}C_{18}^+ + C_2H_2 = H_{11}C_{20}^+ + H_2$	6.0E+14	0.0	0
92	$H_{11}C_{18}^+ + C_4H_2 = C_{22}H_{13}^+$	6.0E+14	0.0	0
93	$H_{11}C_{18}^+ + C_4H_2 = H_{11}C_{20}^+ + C_2H_2$	6.0E+14	0.0	0
94	$H_{11}C_{20}^+ + C_2H_2 = C_{22}H_{13}^+$	6.0E+14	0.0	0
95	$H_{11}C_{20}^+ + C_3H_4 = C_{23}H_{13}^+ + H_2$	6.0E+14	0.0	0
96	$H_{11}C_{20}^+ + C_4H_2 = C_{24}H_{13}^+$	6.0E+14	0.0	0

TABLE III

ION-ELECTRON RECOMBINATION REACTIONS

$$k = AT^n \exp(-E(kJ)/RT), \text{ cm}^3, \text{ mol}, \text{ s}$$

Codes for ion structures: $C_3H_3^+ = C_3H_3^+(l)$; $H_3C_3^+ = C_3H_3^+(c)$; $C_6H_5^+ = C_6H_5^+(\text{linear})$; $C_7H_7^+ = \text{benzyl ion}$; $HC = CH^*$ (electronic state: $^2\Delta$); $C_xH_y^+$, $H_yC_x^+$, and $C_xH_{y-1}H$ represent three different isomers of the same ion.

No.	REACTION			A	n	E, kJ
1	$H_3O^+ + e$	$\rightarrow$	$H_2O + H$	1.3E+19	0.5	0.0
2	$HCO^+ + e$	$\rightarrow$	$CO + H$	7.4E+18	0.69	0.0
3	$CH_3^+ + e$	$\rightarrow$	$CH + H_2$	5.3E+18	0.5	0.0
4	$C_2H_3^+ + e$	$\rightarrow$	$C_2H + H_2$	8.5E+18	0.5	0.0
5	$C_3H_3^+ + e$	$\rightarrow$	$C_2H_2 + CH$	1.1E+19	0.5	0.0
6	$H_3C_3^+ + e$	$\rightarrow$	$C_2H_2 + CH$	1.1E+19	0.5	0.0
7	$C_4H_3^+ + e$	$\rightarrow$	$C_2H_2 + C_2H$	1.2E+19	0.5	0.0
8	$C_4H_5^+ + e$	$\rightarrow$	$C_2H_2 + C_2H_3$	1.2E+19	0.5	0.0
9	$C_5H_3^+ + e$	$\rightarrow$	$C_3H_3 + C_2$	1.3E+19	0.5	0.0
10	$C_5H_3^+ + e$	$\rightarrow$	$C_2H + C_3H_2$	1.3E+19	0.5	0.0
11	$C_7H_5^+ + e$	$\rightarrow$	$C_4H_2 + C_3H_3$	1.5E+19	0.5	0.0
12	$C_6H_5^+ + e$	$\rightarrow$	$C_4H_4 + C_2H$	1.4E+19	0.5	0.0
13	$C_7H_5^+ + e$	$\rightarrow$	$C_5H_5 + C_2$	1.5E+19	0.5	0.0
14	$C_7H_7^+ + e$	$\rightarrow$	$C_6H_4 + CH_3$	1.5E+19	0.5	0.0
15	$C_7H_7^+ + e$	$\rightarrow$	$C_6H_6 + CH$	1.5E+19	0.5	0.0
16	$C_8H_7^+ + e$	$\rightarrow$	$C_6H_6 + C_2H$	1.6E+19	0.5	0.0
17	$C_9H_7^+ + e$	$\rightarrow$	$C_8H_6 + CH$	1.7E+19	0.5	0.0
18	$C_{10}H_9^+ + e$	$\rightarrow$	$C_{10}H_8 + H$	1.8E+19	0.5	0.0
19	$H_9C_{10}^+ + e$	$\rightarrow$	$C_8H_6 + C_2H_3$	1.8E+19	0.5	0.0
20	$C_{11}H_9^+ + e$	$\rightarrow$	$C_{10}H_8 + CH$	1.9E+19	0.5	0.0
21	$H_9C_{11}^+ + e$	$\rightarrow$	$C_8H_6 + C_3H_3$	1.9E+19	0.5	0.0
22	$C_{12}H_9^+ + e$	$\rightarrow$	$C_{12}H_8 + H$	1.9E+19	0.5	0.0
23	$H_9C_{12}^+ + e$	$\rightarrow$	$C_{10}H_8 + C_2H$	1.9E+19	0.5	0.0
24	$C_{13}H_9^+ + e$	$\rightarrow$	$C_{13}H_9$	2.0E+19	0.5	0.0
25	$C_{13}H_9^+ + e$	$\rightarrow$	$C_{12}H_8 + CH$	2.0E+19	0.5	0.0

TABLE III (continued)

No.	REACTION	A	n	E, kJ
26	$C_{14}H_{11}^+ + e \rightarrow C_{14}H_{10} + H$	2.1E+19	0.5	0.0
27	$C_{14}H_{11}^+ + e \rightarrow C_{14}H_{11}$	2.1E+19	0.5	0.0
28	$C_{15}H_{11}^+ + e \rightarrow C_{14}H_{10} + CH$	2.1E+19	0.5	0.0
29	$C_{15}H_{11}^+ + e \rightarrow C_{15}H_{11}$	2.1E+19	0.5	0.0
30	$C_{16}H_{11}^+ + e \rightarrow C_{16}H_{10} + H$	2.2E+19	0.5	0.0
31	$C_{17}H_{11}^+ + e \rightarrow C_{17}H_{10} + H$	2.2E+19	0.5	0.0
32	$C_{17}H_{11}^+ + e \rightarrow C_{16}H_{10} + CH$	2.2E+19	0.5	0.0
33	$H_{11}C_{17}^+ + e \rightarrow C_{17}H_{11}$	2.2E+19	0.5	0.0
34	$H_{11}C_{18}^+ + e \rightarrow C_{16}H_{10} + C_2H$	2.3E+19	0.5	0.0
35	$C_{18}H_{10}H^+ + e \rightarrow C_{18}H_{10} + H$	2.3E+19	0.5	0.0
36	$C_{19}H_{11}^+ + e \rightarrow C_{19}H_{11}$	2.3E+19	0.5	0.0
37	$C_{19}H_{11}^+ + e \rightarrow C_{18}H_{10} + CH$	2.3E+19	0.5	0.0
38	$C_{20}H_{11}^+ + e \rightarrow C_{18}H_{10} + C_2H$	2.4E+19	0.5	0.0
39	$H_{11}C_{20}^+ + e \rightarrow C_{20}H_{11}$	2.4E+19	0.5	0.0
40	$C_{21}H_{11}^+ + e \rightarrow C_{21}H_{11}$	2.4E+19	0.5	0.0
41	$C_{21}H_{11}^+ + e \rightarrow C_{18}H_{10} + C_3H$	2.4E+19	0.5	0.0
42	$C_{22}H_{13}^+ + e \rightarrow C_{22}H_{12} + H$	2.5E+19	0.5	0.0
43	$C_{23}H_{13}^+ + e \rightarrow C_{22}H_{12} + CH$	2.5E+19	0.5	0.0
44	$C_{23}H_{13}^+ + e \rightarrow C_{23}H_{13}$	2.5E+19	0.5	0.0
45	$C_{24}H_{13}^+ + e \rightarrow C_{24}H_{12} + H$	2.5E+19	0.5	0.0
46	$C_{24}H_{13}^+ + e \rightarrow C_{24}H_{12} + H$	2.5E+20	0.5	0.0

TABLE IV

TO ADD TEN CARBON ATOMS BY THE FREE RADICAL MECHANISM

$C_{10}H_8$

$\downarrow$ $\uparrow$ + H•   (– H_2)   0.27 μs

$C_{10}H_7$•

$\downarrow$ + C_2H_2 (– H•)   0.11 μs

$C_{12}H_8$

$\downarrow$ $\uparrow$ + H• (– H_2)   0.64 μs

$C_{12}H_7$•

$\downarrow$ $\uparrow$ + C_2H_2 (– H•)   0.16 μs

$C_{14}H_8$

$\downarrow$ + H • (– H_2)   2.7 μs

$C_{14}H_7$•

$\downarrow$ + C_2H_2 1.1 μs

$C_{16}H_9$•

$\downarrow$ $\uparrow$ cyclizes

$C_{16}H_9$•

$\downarrow$ $\uparrow$ + C_2H_2 (– H•)   1.1 μs

$C_{18}H_{10}$

$\downarrow$ + H • (– H_2)   2.9 μs

$C_{18}H_9$•

$\downarrow$ $\uparrow$ + C_2H_2 (– H•)   0.69 μs

$C_{20}H_{10}$

Total Time = 9.7 μs

TABLE V
TO ADD TEN CARBON ATOMS BY THE IONIC MECHANISM

$C_{11}H_9^+$

$\downarrow$ + C_2H_2 (-H_2)   3.1 μs

$C_{13}H_9^+$

$\downarrow$ ↑   + C_2H_2 0.40 μs

$C_{15}H_{11}^+$

$\downarrow$ + C_2H_2 (- H_2)   0.42 μs

$C_{17}H_{11}^+$

$\downarrow$ + C_2H_2 (- H_2)   1.2 μs

$C_{19}H_{11}^+$

$\downarrow$ + C_2H_2 (- H_2)   0.50 μs

$C_{21}H_{11}^+$

Total Time = 5.6 μs